

To the Grignard reagent from 12 g. of bromobenzene there was added 15 g. of 9-chloro-9-phenylfluorene. A vigorous reaction took place, with evolution of a considerable amount of heat, and with precipitation of a white solid as Schmidt-Nickels reports. After the mixture was refluxed for an hour, this solid was filtered off, washed with water and with acetone and then dried; weight 3.1 g.; m. p. 215–220°. After recrystallization from benzene it was obtained in the form of large needles melting at 219–220°, which were found to be identical with 9,9-diphenylfluorene prepared from *o*-phenyltriphenylcarbinol by dehydration.<sup>9</sup>

### Summary

The system  $\text{Mg} + \text{MgBr}_2$  (or  $\text{MgI}_2$ ) reacts with phenylbiphenylene-methyl and gives the Grignard reagent, phenylbiphenylenemethylmagnesium bromide,  $2(\text{C}_6\text{H}_4\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{C} + \text{Mg} + \text{MgX}_2 = 2(\text{C}_6\text{H}_4\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{CMgX}$ .

The same Grignard reagent is formed from the action of magnesium on phenylbiphenylenebromomethane. This reaction was found to take place in two successive stages: (a) formation of phenylbiphenylenemethyl and  $\text{MgBr}_2$ ; (b) reaction of the radical with  $\text{Mg} + \text{MgBr}_2$ .

The Grignard reagent was isolated in crystalline state and found to have the composition assigned to it. The compound was converted by water into phenylfluorene; by carbon dioxide into phenylbiphenylene-acetic acid.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

## THE SUPPOSED EXISTENCE OF TWO STEREOISOMERIC 9-BENZYL-9-PHENYLFLUORENES

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Among the examples of a new kind of stereoisomerism, Schlenk and Bergmann<sup>1</sup> report an isomer of 9-benzyl-9-phenylfluorene. The latter compound was prepared by Gomberg and Cone<sup>2</sup> from benzylmagnesium chloride and 9-chloro-9-phenylfluorene; their product crystallized in prisms and melted at 136°. Schlenk and Bergmann allowed benzyl chloride to react with 9-sodium-9-phenylfluorene and obtained leaflets melting at 125–126°, which they consider to be a stereoisomeric 9-benzyl-9-phenylfluorene. Recently, however, Schmidt, Stein and Bamberger<sup>3</sup> were unable to obtain this isomer when following the directions given for

<sup>9</sup> Ullmann and von Wurstemberger, *Ber.*, **38**, 4106 (1905); Clarkson and Gomberg, *THIS JOURNAL*, **52**, 2881 (1930).

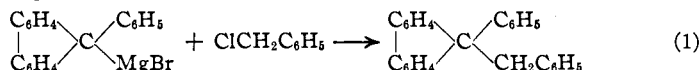
<sup>1</sup> Schlenk and Bergmann, *Ber.*, **62**, 745 (1929).

<sup>2</sup> Gomberg and Cone, *ibid.*, **39**, 2968 (1906).

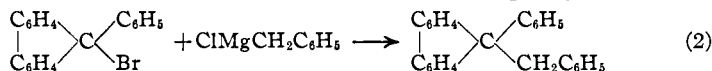
<sup>3</sup> Schmidt, Stein and Bamberger, *ibid.*, **62**, 1890 (1929).

its preparation. In phenylbiphenylenemethylmagnesium bromide<sup>4</sup> we have a close analog of the sodium derivative of Schlenk and Bergmann, and its reaction with benzyl chloride was studied in order to determine whether a low-melting compound would be formed when using it instead of the sodium derivative.

Phenylbiphenylenemethylmagnesium bromide reacts readily with benzyl chloride and gives 9-benzyl-9-phenylfluorene



This compound was found to be identical with the product obtained from benzylmagnesium chloride and 9-chloro- or 9-bromo-9-phenylfluorene



The product crystallized from ligroin in the form of prisms and melted at 138–138.5°.

The directions of Schlenk and Bergmann were then followed in an attempt to prepare the isomer. However, from 9-sodium-9-phenylfluorene and benzyl chloride there was obtained a 99% yield of the high-melting compound; no trace of a low-melting isomer was found. The compound was identical in melting point and in crystal form<sup>5</sup> with the products obtained above (Equations 1 and 2).

### Experimental

**Benzylmagnesium Chloride + 9-Bromo-9-phenylfluorene.**—To a filtered solution of benzylmagnesium chloride prepared from 10 g. of benzyl chloride, 8.05 g. of 9-bromo-9-phenylfluorene was added. The mixture was heated for six hours and then hydrolyzed. From the ether solution was obtained 5 g. of 9-benzyl-9-phenylfluorene. After recrystallization from *n*-propyl alcohol the compound melted at 136–136.5°. The melting point was raised to 138–138.5° (corr. 140.3–140.8°) by treatment of an acetic acid solution with a small amount of chromic acid. The color was removed from the product by treatment with concentrated sulfuric acid and the substance was then recrystallized from acetic acid. From ligroin the compound was obtained in the form of large transparent crystals.

**Phenylbiphenylenemethylmagnesium Bromide + Benzyl Chloride.**—Five grams of benzyl chloride was added to the Grignard reagent prepared from 3.22 g. of 9-bromo-9-phenylfluorene, and the resulting mixture was heated for three hours; during this time a large amount of magnesium chloride precipitated. After hydrolysis, 2 g. of 9-benzyl-9-phenylfluorene was obtained. Recrystallization from ligroin gave large prisms melting at 136–137°. After the chromic acid purification the melting point was 138–138.5° (corr. 140.3–140.8°). The Grignard reagent was also prepared from crystalline phenylbiphenylenemethyl and Mg + MgBr<sub>2</sub>; with benzyl chloride a product was obtained which after recrystallization from ligroin melted at 137.5–138.0°.

**Benzyl Chloride + 9-Sodium-9-phenylfluorene (Method of Schlenk and Berg-**

<sup>4</sup> Bachmann, THIS JOURNAL, 52, 3287 (1930).

<sup>5</sup> This comparison was made by Dr. C. B. Slawson of the Mineralogy Department, and thanks are extended to him again at this time.

mann).—Phenylfluorenol methyl ether was prepared according to the directions of Schlenk and Bergmann.<sup>6</sup> However, while they report fluorescence of the solution of the methyl ether, no trace of such fluorescence was shown by our solutions.

Five grams of sodium powder was allowed to react with 10 g. of 9-phenylfluorenol methyl ether in 150 cc. of absolute ether in a sealed flask. In less than half an hour the solution was red in color. When the reaction was complete the mixture was treated with benzyl chloride (3 cc.) until no more red sodium derivative remained. The mixture was hydrolyzed, the ether solution was well washed with water and the solvent was then removed under reduced pressure. The crystalline residue was digested with cold methyl alcohol and filtered; weight 11.10 g.; m. p. 136–136.5°. From the alcoholic filtrate an additional 0.32 g. was isolated, making the total yield equivalent to 99%. After being recrystallized from *n*-propyl alcohol, acetic acid or ligroin, the crystals melted at 138–138.5° (corr. 140.3–140.8°). When mixed with 9-benzyl-9-phenylfluorene made by the other methods the melting point remained the same.

In another experiment the mixture of the reactants was kept cold, and after hydrolysis the reaction product was obtained by allowing the ether to evaporate at room temperature. Only the compound melting at 138–138.5° was obtained.

### Summary

9-Benzyl-9-phenylfluorene as prepared from phenylbiphenylenemethylmagnesium bromide and benzyl chloride is identical with the product formed by interaction of 9-bromo-9-phenylfluorene and benzylmagnesium chloride. Furthermore, the same compound was obtained in 99% yield from the action of benzyl chloride on 9-sodium-9-phenylfluorene, and no low-melting isomer was produced in this reaction.

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[CONTRIBUTION NO. 35 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS AND COMPANY]

## STUDIES ON POLYMERIZATION AND RING FORMATION. V. GLYCOL ESTERS OF OXALIC ACID

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Melting points ranging from 110 to 172° have been ascribed to ethylene oxalate.<sup>1</sup> Bischoff,<sup>2</sup> by distillation, prepared a form melting at 142–143°, which he showed to be monomeric. He observed that the melting points of this and higher-melting forms change spontaneously on standing, and he ascribed this change to reversible polymerization but without the support of any comparative molecular weight data. In connection with a study of glycol esters of dibasic acids<sup>3</sup> we have made some further observations

<sup>6</sup> Schlenk and Bergmann, *Ann.*, **463**, 202 (1928).

<sup>1</sup> (a) Bischoff, *Ber.*, **27**, 2939 (1894); (b) **40**, 2803 (1907); (c) Adams and Weeks, *THIS JOURNAL*, **38**, 2518 (1916); (d) Tilitcheev, *Ber.*, **56**, 2218 (1923).

<sup>2</sup> Bischoff, *ibid.*, **40**, 2803 (1907).

<sup>3</sup> Carothers and Arvin, *THIS JOURNAL*, **51**, 2560 (1929); Carothers and Van Natta, *ibid.*, **52**, 314 (1930); Carothers and Dorough, *ibid.*, **52**, 711 (1930).